International Journal of ELECTROCHEMICAL SCIENCE www.electrochemsci.org

Preparation of Sulphur-Doped Graphene-Based Electrodes by Cyclic Voltammetry: A Potential Application for Vanadium Redox Flow Battery

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Received: 21 October 2017 / Accepted: 24 November 2017 / Published: 16 December 2017

A new, simple and green method was proposed for preparation of the S-doped graphene based pencil graphite electrodes (S-GPGEs) in sulfuric acid solution by cyclic voltammetric method in this work. The obtained S-GPGEs were investigated by the measurements of scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and electrochemical performance. The results show that the S-GPGEs were composed of many nano flakes. –C-S-C- and –C-SOx-C- (x:2, 3) groups were determined by XPS. Raman spectra were taken to determine the optical properties of the electrodes. Thus, the results show that S-doped graphene was obtained in situ. S-GPGEs were used as positive electrode components of a vanadium redox flow battery (VRB). The electrodes showed great electrochemical activity in the positive electrolyte of VRB. This novel method is easy, cheap and environmentally friend for production of S-doped graphene for many application such as sensor, electro-optics, energy storage devices and etc.

Keywords: Graphene, Vanadium Redox Flow Battery, Cyclic Voltammetry, S-Doped Graphene, Graphene electrode

1. INTRODUCTION

Graphene, which consists of 2D planar sheets of sp²-bonded carbon atoms as its main structure, was discovered in 2004 [1]. Since the graphene based materials have amazing optical, mechanical and physical properties, they have been used in many different applications such as energy storage devices, sensors, optics and etc. [2–4]. Doping of graphene based materials by hetero atoms like –N and –S improved the many properties of them such as physical, chemical, electrochemical, optical and catalytic [5–9]. The electrode technology is key part of many applications [2–4]. N-doped graphene

electrodes were also used in vanadium redox batteries (VRBs) [10–12]. The doping by –N including groups of graphene was done by chemical methods in most of these studies [10–12]. To be best our knowledge, there are no report about the using of S-doped electrode materials in VRB system.

The preparation of S-doped graphene can be done by chemical, chemical vapor deposition, thermal, and electrochemical exfoliation methods [13–16]. The precipitation of S-doped graphene powder was done in the electrochemical exfoliation method for preparation of S-doped graphene [13]. The process have secondary steps such as filtration, purification, and immobilization for preparation of S-doped graphene based electrode and the preparation of exfoliated graphene takes long time [13]. Chemical vapor deposition is another method for preparation of S-doped graphene [14]. The preparation of S-doped graphene requires high temperature application, catalyst, and inert gas circulation which also bring extra cost [14]. Besides, separation, purification and immobilization steps also have extra time cost for the method [14]. Chemical and thermal synthesis are also used for S-doped graphene preparation [15-16]. The used chemicals in these methods bring impurities on the structure of S-doped graphene. Besides, the purification, separation, filtering and drying process take long time in the preparation of S-doped graphene [15-16]. One-step electrochemical preparation of S-doped graphene based material by cyclic voltammetry was reported in our previous study [4]. The preparation of S-doped graphene based material by cyclic voltammetry in one-step can bring a new approach for applications of these materials.

In this work, a novel approach was brought for preparation of S-doped graphene in one-step. Sdoped graphene based electrodes were prepared on a pencil graphite electrode (PGE) in one step. PGE was converted directly into S-doped graphene electrode by cyclic voltammetric method. By arranging the scanned potential in -1.0-(+1.9) V, the graphene was modified with $-SO_x$ and -C-S-C groups. The electrodes were characterized by spectroscopic and microscopic methods such as XPS, Raman and SEM. S-doped graphene coated electrodes were used as positive electrodes of vanadium redox battery. S-doped graphene based electrode showed great electrochemical activity as positive electrode of VRB.

2. MATERIALS AND METHODS

2.1. Electrochemical production of S-GPGEs

Cyclic voltammetric method was used for preparation of S-doped graphene based electrode. A PGE was treated electrochemically in sulfuric acid solutions in the potential ranges of -1.0-(+1.9), -0.4-(+1.9), 0.8-(+1.9), and 1.4-(+1.9) V versus Ag/AgCl (in 3 M KCl) with 50 cycles at a 50 mV/s scan rate at room temperature (25 °C) and prepared S-doped electrodes were called as S-GPGE1, S-GPGE2, S-GPGE3, and S-GPGE4, respectively. The S-GPGEs were washed with deionized water to remove impurities and dried at room temperature before the electrochemical measurements [4,17,18].

2.2. Spectroscopic and morphological characterization of electrodes

SEM (Carl Zeiss Ultra Plus FESEM) analysis were carried out to determine the morphological features of PGE during the electrochemical treatment at different magnifications (50000x) after

applying an Au 40 mA current for 30 s. Raman spectroscopic analysis for S-GPGEs were done with a Bruker Optics FT-Raman Scope III system using a 532 nm laser. Thermo Scientific K-Alpha model XPS using an Al anode (Al Ka = 1468.3 eV) controlled by the Avantage 5.934 software. The angle between the photoelectron detector lens and the surface was 90°.

2.3. VRB application of S-doped graphene electrodes

S-GPGEs were used as positive electrode component of VRB. The electrolyte solution (2.0 M of V(IV)) was prepared dissolution of VOSO₄ (Sigma-Aldrich, >97%) in 5.0 M sulfuric acid (Sigma-Aldrich, >95-98%). Positive electrolyte solutions of VRB were characterized by cyclic voltammetric analysis in a potential range of 0.45 - 1.45 V versus SCE with S-GPGEs as working electrodes. Counter electrode was platinum wire. The scanning rate was 50 mV.s⁻¹ for cyclic voltammetric analysis in VRB application.

3. RESULT AND DISCUSSION

3.1. Preparation and Characterization of S-GPGEs

One-step electrochemical preparation of graphene coated electrodes in nitric acid solution by cyclic voltammetric method was reported in our previous work [4]. In this work, S-doped graphene coated electrodes in sulfuric acid solution were prepared in one-step by cyclic voltammetric method with scanning of different potential ranges. Fig. 1a shows the 1st, 3rd, 5th, 10th, 30th and 50th voltammetric cycle of PGE in 5.0 M of sulfuric acid between -1.0 - (+1.9) V versus Ag/AgCl. Certain oxidation peaks at 1.50 V, 1.75 V, 0.20 V and reduction peaks at 1.30 V, 1.00 V, -0.25 V were observed in cyclic voltammograms (Fig. 1a). Obtained oxidation peaks probably related with the covalently bonded -S and -O groups on the electrode surface [4,19]. The reduction peaks also related with reduction of oxygen and sulfur including functional groups [4]. Since the formed graphene layers on the PGE surface during the increasing cycle increased electrochemically active surface areas of PGE, certain increases were observed in anodic and cathodic peaks from 1st to 50th cycle (Fig. 1a) [4]. XPS analysis were carried out to determine the chemical structure of S-GPGE1. Fig. 1b and 1c show the S2p and C1s spectra of S-GPGE1, respectively. The certain peaks at 163.9 eV and 165.2 eV were corresponding of -C-S-C- structure which were obtained in reduction of oxidized surface of PGE with -S and -O including functional groups (Fig. 1a and 1b) [15,20-22]. The peaks obtained between 167.5 eV and 171.5 eV represent the $-C-SO_x-C-(x:2, 3)$ groups on the graphene formed surface of PGE (Fig. 1c) [15,20–22]. Raman spectra were taken to determine the optical properties of S-GPGE1 (Fig. 1d). Obtained peaks around of 1346, 1576, and 2698 cm⁻¹ represent the D, G and 2D bands, respectively [4]. The D peak was related the doping of graphitic sheets, and large amount of topological defects due to -S doping [20,23,24]. Tuinstra and Koenig's equation (Eq. 1) was used for calculating the average size of the sp² domain or cluster diameter (*L*a) which was inversely proportional to the rate of I_D/I_G [20,23,24]. La value was calculated as 120.5 for S-GPGE1 indicating 47 sp² carbon rings for graphene layers. The 2D peak also supported the formation of few layers graphene [20,23,24]. The transparent structure of S-GPGE1 can be seen in Fig. 1e. The surface of PGE consisting of graphitic flakes changed during the cyclic voltammetric treatment and a few layered S-doped graphene formed on the PGE surface (Fig. 1e) [4]. This also shows the success of S-doping on the graphene coated surface of PGE.

$I_{\rm D}/I_{\rm G} = C(\lambda)/L\alpha.$ (1)

To determine the effects of applied potential on the formation of S-doped graphene by cyclic voltammetry, narrower potential ranges were studied as (-0.4;1.9 V), (0.8;1.9 V) and (1.4;1.9 V). Fig. 2a shows the cyclic voltammograms of PGE in a potential range of -0.4 and 1.9 V from 1st cycle to 50th cycle. The obtained oxidation peaks at around of 1.50 V, 1.75 V and 0.30 V represent the formation of functional groups consisting of –S and –O atoms on the surface of PGE (Fig. 2a) [4,19]. These oxidized species on the surface of PGE reduced at 1.25 and 0 V while the graphene layers were forming on the PGE surface (Fig. 2a) [4]. Increasing anodic and cathodic peaks currents from 1st to 50th cycle was probably related with increasing electrochemically active surface area of formed graphene layers on the PGE [4]. When the C1s and S2p XPS spectra of S-GPGE2 were analyzed, the formation of –C-S-C and –C-SO_x-C- were determined on the graphene formed surface of PGE (Fig. 2b and 2c) [15,20–22]. However, a certain decrease for –C-S-C- peak was determined in the S2p spectra of S-GPGE2. This result was probably caused by not completed reduction of –C-SOx-C- including functional groups due to narrower applied potential in the formation of S-GPGE2 (Fig. 1b and 2b).





Figure 1. a) Cyclic voltammograms of PGE in 5.0 M of sulfuric acid, b) S2p XPS spectra of S-GPGE1, c) C1s XPS spectra of S-GPGE1, d) Raman spectra of S-GPGE1 and e) 50000× SEM picture of S-GPGE1





Figure 2. a) Cyclic voltammograms of PGE in 5.0 M of sulfuric acid, b) S2p XPS spectra of S-GPGE1, c) C1s XPS spectra of S-GPGE2, d) Raman spectra of S-GPGE2 and e) 50000× SEM picture of S-GPGE2

Raman spectra of S-GPGE2 were shown in Fig. 2d. Calculated *L*a value was 220 indicating 86 sp^2 carbon rings for graphene layers [20,23,24]. Here, formed layers of graphene in S-GPGE2 were higher than that of S-GPGE1's. The SEM pictures also supported to the formation of graphene layers on the surface of PGE during cyclic voltammetric treatment (Fig. 2e).

Fig. 3a shows the 1st, 3rd, 5th, 10th, 30th and 50th cycle obtained during the preparation of S-GPGE3 by cyclic voltammetry. The anodic and cathodic peaks in cyclic voltammograms were probably related with the oxidation of PGE by oxygen and sulfur including functional groups [4,19]. In contrast to S-GPGE1 and S-GPGE2, only one reduction peak was observed in the cyclic voltammograms (Fig. 2a). This showed that the reduction of oxidized surface of PGE was not fully completed in the studied potential range. C1s and S2p XPS spectra of S-GPGE3 also supported the not fully completed reduction of functional groups consisting of oxygen and sulfur (Fig. 3b and 3c). Especially, obtained –C=O peak at 288.9 eV in the C1s spectra supported the formation of unreduced functional groups on the surface of S-GPGE3 (Fig. 3c). Besides, the intensity of –C-S-C- peak in S-GPGE3 was lower than those of S-GPGE1 and S-GPGE2 (Fig. 1b, 2b and 3b). *L*a value was also calculated using of Eq. 1 in the Raman spectra of S-GPGE3, which was 97 indicating of 38 sp² bonded carbon rings (Fig. 3d) [20,23,24]. This was also lower than those of S-GPGE2 due to applied lower potential range in the preparation process of S-GPGE3. The surface of PGE including S-doped graphene can be seen easily in the Fig. 3e.

The narrowest potential range was applied for the preparation of S-GPGE4. The obtained cyclic voltammograms in the preparation of S-GPGE4 were shown in Fig. 4a. The anodic and cathodic peaks in the voltammograms were corresponding the formation of functional groups consisting of –S and –O atoms [4,19]. Since the narrowest potential range was applied in the preparation of S-GPGE, the formed functional groups on PGE surface were not fully reduced.



Figure 3. a) Cyclic voltammograms of PGE in 5.0 M of sulfuric acid, b) S2p XPS spectra of S-GPGE1, c) C1s XPS spectra of S-GPGE3, d) Raman spectra of S-GPGE3 and e) 50000× SEM picture of S-GPGE3



Figure 4. a) Cyclic voltammograms of PGE in 5.0 M of sulfuric acid, b) S2p XPS spectra of S-GPGE4, c) C1s XPS spectra of S-GPGE4, d) Raman spectra of S-GPGE4 and e) 50000× SEM picture of S-GPGE4

While the peak intensity of $-C-SO_x-C$ - in the S2p XPS spectra of S-GPGE4 increased, intensity of -C-S-C- peak decreased (Fig. 4b). This result also showed the importance of the effects of applied

potential on the formation of -S doped graphene on the surface of pencil graphite electrode. Obtained -C=O peak in the C1s XPS spectra of S-GPGE4 supported the uncompleted reduction of oxygen including functional groups (Fig. 4c) [4]. *L*a value was 80 for S-GPGE4 indicating forming of almost 31 sp² bonded carbon rings on the surface of PGE (Fig. 4d) [20,23,24]. This value was the lowest in the prepared S-doped graphene coated electrodes, and probably caused by applied the narrowest potential range as 1.4-1.9 V versus Ag/AgCl. The formed S-doped graphene was shown in the SEM picture of S-GPGE4 (Fig. 4e)

3.2. VRB Application of S-GPGEs

Prepared S-doped graphene coated electrodes (S-GPGEs) were used as positive electrodes of a vanadium redox flow battery. In this concept, cyclic voltammetric characterization of positive electrolyte solution (2.0 M of V(IV)) of VRB was done in a potential range 0.45-1.45 V versus SCE with 50 mV.s⁻¹ scanning rate.



Figure 5. a) Cyclic voltammograms b) anodic peak currents and c) cathodic peak currents of PGE, S-GPGE1, S-GPGE2, S-GPGE3 and S-GPGE4 in the solution consisting of 2.0 M of V(IV) and 5.0 M of sulfuric acid

The anodic and cathodic peaks which were obtained in cyclic voltammograms at around of 1.05 and 0.85 V represent the redox reactions of V(IV)/V(V) and V(V)/V(IV), respectively (Fig. 5a) [4,25–27]. S-GPGEs showed great electrochemical activity as positive electrode of VRB (Fig. 5a). Anodic and cathodic peaks currents and capacities were the highest in S-GPGE1 and S-GPGE2 (Fig. 5b and 5c). This was also probably related with higher electrochemically active surface area in S-GPGE1 and S-GPGE2. Formed number of graphene was higher in S-GPGE1 and S-GPGE2 than those of S-GPGE3 and S-GPGE4 according to results of Raman spectra analysis (Fig. 1d, 2d, 3d and 4d). The defects sides generated in S-GPGEs showed more electrochemically active sides than PGE [4,28]. According to the result of electrochemical analysis, S-doped graphene coated electrodes can be used as positive electrodes of VRB.

4. CONCLUSION

This novel one-step electrochemical method for the preparation of an S-doped graphene-based electrode is easy to use, low cost, and environmentally friendly. By the changing of applied potential, the functional modification of graphene coated surface of PGE was achieved. Surface modification of graphene electrodes were done by -C-S-C- and $-C-SO_x-C-$ groups. The formation of S-doped graphene on the PGE surface was confirmed by spectroscopic and microscopic analysis. Besides, applications of S-GPGEs were studied for positive electrolyte of VRB. The electrochemical activities of S-GPGEs were higher than that of PGE. Since the graphene based materials have brought a new approach for carbon based materials, production of them by this method can open many application areas for S-doped graphene.

ACKNOWLEDGEMENT

This work was supported by the Yildiz Technical University Scientific Projects Coordination Department (Project number: 2014-01-02-DOP06). Hurmus Gursu and Metin Gencten express their gratitude to Tubitak-BIDEB for the fellowship. The authors would like to thank Dr. M. Baris Yagci for the XPS analysis.

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